

Preliminary communication

New aspects of the formation of the primary product of the Fischer–Hafner synthesis under standard laboratory conditions: crystal structure of  $[(C_6H_6)_2Cr][Al_3OCl_8]$ <sup>1</sup>

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Abstract

One reaction product of the first step of the bis(benzene)chromium synthesis with commercially available and not further purified compounds leads to the formation of bis(benzene)chromium octachlorooxotri-aluminate  $[(C_6H_6)_2Cr][Al_3OCl_8]$ . The structure of this compound has been confirmed by X-ray diffraction.

*Keywords:* Crystal structure; Aluminium; Arene; Chromium; X-ray diffraction; Halooxometallate

1. Introduction

Bis(benzene)chromium surely is one of the most prominent compounds of organometallic chemistry. Although intense attempts have been made to clarify the structural properties of the intermediate product of the Fischer–Hafner synthesis the results have not been completely satisfying [1]. In the corresponding paper, Fischer and Seeholzer carried out extensive research under rigorous (!) exclusion of oxygen; they varied all parameters of the synthesis and gave elemental analyses as supporting evidence. Their results concerning the primary product showed a composition of the crystalline solid of Cr:Al:Cl:benzene = 1:2.37:7.6: < 2.

Dealing with bis(benzene)chromium chemistry, we wondered what would be the primary product of the Fischer–Hafner synthesis under less rigorous exclusion of oxygen, using commercially available and not further purified starting materials.

In this paper we report the characterization and X-ray structure of  $[(C_6H_6)_2Cr][Al_3OCl_8]$  (1).

2. Experimental section

All experiments were performed under dinitrogen in solvents purified by standard methods.  $AlCl_3$ ,  $CrCl_3$  (Aldrich) and aluminium (Merck) were used without further purification. IR spectra were recorded on a Perkin–Elmer FT 842 spectrometer.

2.1. Synthesis of bis(benzene)chromium octachlorooxotri-aluminate (1)

We followed the instructions of Fischer and Seeholzer [1] for the reflux method using 0.5 g (3.2 mmol)  $CrCl_3$ , 0.1 g (3.7 mmol) Al powder, 1.2 g (9 mmol)  $AlCl_3$ , 10 ml benzene and 5  $\mu$ l mesitylene. After 35 h the reaction mixture was strained and the benzene phase removed. The remaining orange solution was kept at room temperature for about 4 weeks. After removing the liquid, washing with absolute benzene and drying in vacuo, 0.23 g (17%) yellow crystals were obtained. M.p: 92–94°C. IR (CsI pellet):  $\nu$  1601s, br, 1570s, br, 1352s, 1338s, 1098w, br, 1002vw, br, 818m, br, 757m, 674m, br, 614m, br, 480w, sh, 460w, sh, 421w  $cm^{-1}$ .

2.2. Crystal structure determination of 1

$C_{12}H_{12}Al_3Cl_8CrO$ , molecular weight 640.8  $g\ mol^{-1}$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 890.3(1)$ ,  $b = 1776.9(3)$ ,  $c =$

<sup>1</sup> Dedicated to my teacher Professor Dr. G.E. Herberich on the occasion of his 60th birthday.

755.1(2) pm,  $\alpha = 95.30(1)$ ,  $\beta = 108.22(1)$ ,  $\gamma = 94.28(1)^\circ$ ,  $Z = 2$ ,  $V = 1.1230(7) \text{ nm}^3$ ,  $d_{\text{calc}} = 1.895 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 20.26 \text{ cm}^{-1}$ . Diffraction data were collected with an Enraf–Nonius CAD4-diffractometer at 203 K, Mo K $\alpha$  radiation (graphite monochromator,  $\lambda = 71.07 \text{ pm}$ ), crystal size  $0.5 \times 0.45 \times 0.3 \text{ mm}$ ,  $\omega$ -scans ( $3 < \theta < 27^\circ$ ). All data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied based on azimuthal scans, using the SDP system of programs [2]. Of the 5029 data collected, 4221 were unique with intensities  $I > 1\sigma(I)$  and only these were used in the structure solution and refinement. The structure was solved by direct methods (SHELXS-86) [3] and difference Fourier maps. Positions for all hydrogen atoms were treated as riding with isotropic thermal parameters of  $B_{\text{H}} = 1.3B_{\text{C}}$ . Convergence was obtained for 230 parameters with the agreement factors  $R = 0.045$  and  $R_w = 0.061$ , using statistical weights  $w = 1/\sigma^2(F_o)$ . The final difference Fourier map showed a maximum of residual electron density of  $0.57 \times 10^{-6} \text{ e pm}^{-3}$ . Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405215.

### 3. Results and discussion

According to the reflux method of the experimental instructions of Fischer and Seeholzer [1], filtering the primary reaction mixture from the solid we obtained  $[(\text{C}_6\text{H}_6)_2\text{Cr}][\text{Al}_3\text{OCl}_8]$  (**1**) in a reproducible reaction. Traces of humidity and with hydroxide-contaminated  $\text{AlCl}_3$  are probably responsible for the formation of **1**. Yellow crystals were obtained after several weeks at room temperature. The compound crystallizes in the triclinic space group  $\bar{P}1$ .

The chromium atoms were found on special positions in the unit cell, generating two bis(benzene)chromium molecules with eclipsed benzene rings, as generally observed in solid-state structures of  $[\text{Cr}(\eta^6\text{-arene})_2]$  complexes [4] (Fig. 1).

The chromium–ring distances are comparable with literature values (160 and 161 pm) [4] (Table 1).

The central oxygen atom of the chlorooxoaluminate counterion (Fig. 2) is bonded to a terminal  $\text{AlCl}_3$  group and takes part in a four-membered ring together with two  $\text{AlCl}_2$  groups and a chlorine atom. It is almost planar surrounded by the aluminium atoms with equal Al–O bond distances. Earlier results from Thewaldt and Stollmaier present an  $[\text{Al}_3\text{OCl}_8]$ -containing complex in a different conformation [5]. The oxygen is coordinated similarly, but two unsymmetric Al–Cl–Al bridges (218/219 and 273/263 pm) lead to the formation of a pentacoordinated aluminium atom. The bond distances for Al–O in both complexes are very similar (177.2 for **1** and 176.5 pm in the literature [5]).

Three types of Al–Cl bond can be found in the structure of **1** with significantly different distances. In the  $\text{AlCl}_3$ -fragment they amount to an average value of 212 pm. These bond lengths fall within the range which has been found for  $[\text{AlCl}_4]^-$  complexes (212–214 pm) [6]. The Al–Cl distances at the four-membered ring are 208 pm; comparable distances can be observed in  $\text{Al}_2\text{Cl}_6$  (206 pm) [7] and  $[\text{Al}_2\text{Cl}_7]^-$  (208 pm) [8]. The Al–Cl(8) distances are 227 and 230 pm. Similar bond lengths for Al–Cl chlorine bridges can be found in  $[\text{Al}_2\text{Cl}_7]^-$  (227 pm) [8] and  $\text{Al}_2\text{Cl}_6$  (221 pm) [5,7]. The four-membered Al–O–Al–Cl ring shows some deformation, considering the Al(2)–O–Al(3) angle ( $107.43(9)^\circ$ ) and the remarkably acute Al(2)–Cl(8)–Al(3) angle with  $77.90(3)^\circ$  (Table 2)!

Considering the weaker interactions, one can find intermolecular contacts between the chlorine atoms of the aluminates (Table 3). With the 4 Å chlorine rule as a basis [9] there are two or three  $\text{Cl} \cdots \text{Cl}$  contacts for

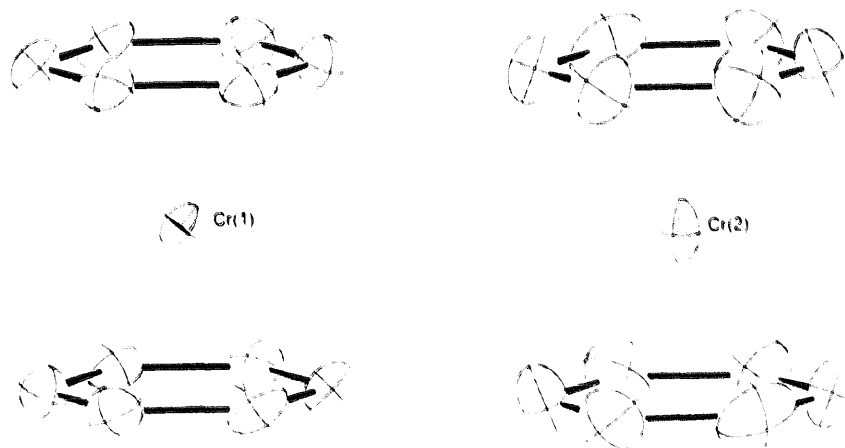


Fig. 1. Molecular structure of the bis(benzene)chromium cations, chromium atoms on  $\bar{1}$  (second benzene rings generated). Displacement ellipsoids are at the 30% probability level, hydrogen atoms omitted.

Table 1  
Selected bond distances (pm)

Cr1–C(ring1)	212.8(2)–214.4(2)	C–C(ring 1)	139.7(4)–141.5(4)
Cr2–C(ring2)	210.0(3)–213.1(3)	C–C(ring 2)	137.8(5)–141.3(6)
Al(1)–O	177.4(2)	Al(2)–Al(3)	286.0(1)
Al(1)–Cl(1)	211.05(9)	Al(3)–O	177.6(2)
Al(1)–Cl(2)	209.86(9)	Al(3)–Cl(6)	208.52(9)
Al(1)–Cl(3)	213.58(9)	Al(3)–Cl(7)	207.45(9)
Al(2)–O	177.2(2)	Al(3)–Cl(8)	230.6(1)
Al(2)–Cl(4)	208.68(9)	Cl(3)–O	296.1(2)
Al(2)–Cl(5)	208.52(8)	Cl(8)–O	280.5(2)
Al(2)–Cl(8)	224.27(9)		

each chlorine atom with distances from 363.6(1) to 392.9(1) pm. These contacts determine the formation of a layer structure parallel to the *ac*-plane and may be the reason for a slight deformation in the chlorooxoaluminate.

The IR spectra of **1** have been recorded in the solid state with a CsI pellet. Comparing these results with the IR of AlOCl in the range of 1000–400 cm<sup>-1</sup>, we found similar bands at 818, 757 and 674 cm<sup>-1</sup> (AlOCl: 825, 725, 690 cm<sup>-1</sup> [10] and 825, 710 and 680 cm<sup>-1</sup> [11]). Absorptions at 480 and 460 cm<sup>-1</sup> can be attributed to  $\nu$  (Al–Cl), as found in AlCl<sub>3</sub><sup>-</sup>-containing compounds (474 or 485 cm<sup>-1</sup>) [12].

Comprehensive IR and Raman studies in solution were carried out by Berg and Østfold [13]. Their results indicate the formation of [Al<sub>3</sub>OCl<sub>8</sub>]<sup>-</sup> ions together with other chlorooxoaluminates. Evidence for their formation has also been discussed by Zawodzinski and Osteryoung, who give <sup>17</sup>O NMR spectra as supporting data [14].

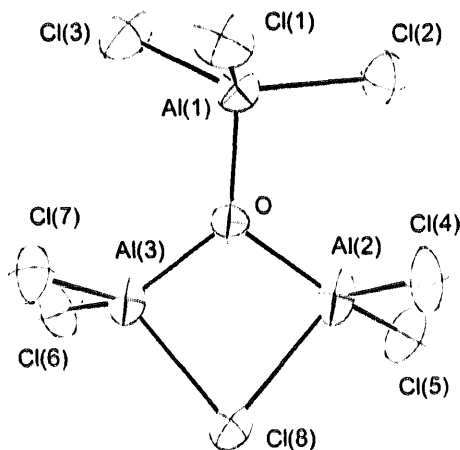


Fig. 2. Molecular structure of the octachlorooxotrialuminate anion. Displacement ellipsoids are at the 30% probability level.

Table 2  
Selected bond angles (deg)

Cl(1)–Al(1)–O	108.32(6)	Cl(7)–Al(3)–O	115.31(6)
Cl(2)–Al(1)–O	108.01(6)	Cl(7)–Al(3)–Cl(8)	108.25(4)
Cl(3)–Al(1)–O	98.04(6)	Cl(8)–Al(2)–O	87.83(6)
Cl(4)–Al(2)–O	113.63(6)	Cl(8)–Al(3)–O	85.79(6)
Cl(4)–Al(2)–Cl(8)	111.98(4)	Al(1)–O–Al(2)	130.90(9)
Cl(5)–Al(2)–Cl(8)	112.98(4)	Al(1)–O–Al(3)	121.62(9)
Cl(5)–Al(2)–O	110.48(6)	Al(2)–O–Al(3)	107.43(9)
Cl(6)–Al(3)–O	118.89(6)	Al(2)–Cl(8)–Al(3)	77.90(3)
Cl(6)–Al(3)–Cl(8)	104.57(4)		

Table 3  
Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

Atom	x	y	z	B <sub>eq</sub>
Cl(1)	-0.0123(1)	-0.35052(5)	-0.8181(1)	4.60(2)
Cl(2)	0.35069(9)	-0.27136(5)	-0.4951(1)	4.21(2)
Cl(3)	0.0703(1)	-0.14872(5)	-0.7251(1)	4.14(2)
Cl(4)	-0.0003(1)	-0.41066(4)	-0.3018(1)	3.97(2)
Cl(5)	0.25381(9)	-0.24916(5)	-0.0309(1)	3.70(2)
Cl(6)	-0.0515(1)	-0.06840(5)	-0.3404(1)	4.23(2)
Cl(7)	-0.3296(1)	-0.20409(5)	-0.6851(1)	4.48(2)
Cl(8)	-0.16992(9)	-0.24004(5)	-0.2111(1)	3.73(2)
Al(1)	0.1111(1)	-0.25600(5)	-0.6230(1)	2.89(2)
Al(2)	0.0431(1)	-0.29250(5)	-0.2427(1)	2.74(2)
Al(3)	-0.1253(1)	-0.18172(5)	-0.4531(1)	3.36(2)
O	0.0208(2)	-0.2453(1)	-0.4446(3)	2.77(4)
Cr(1)	0.500	0.000	0.000	2.53(1)
Cr(2)	0.500	0.500	0.000	3.34(2)
C(1)	0.2985(4)	-0.0163(2)	0.0923(5)	3.95(7)
C(2)	0.3084(4)	0.0570(2)	0.0410(5)	3.82(7)
C(3)	0.4504(4)	0.1061(2)	0.1175(5)	4.00(7)
C(4)	0.5822(4)	0.0808(2)	0.2463(5)	4.07(8)
C(5)	0.5723(4)	0.0073(2)	0.2983(5)	4.09(8)
C(6)	0.4309(4)	-0.0417(2)	0.2231(5)	4.04(7)
C(7)	0.4013(6)	0.4369(3)	0.1664(7)	6.5(1)
C(8)	0.3189(5)	0.5007(3)	0.1289(7)	6.0(1)
C(9)	0.4038(6)	0.5718(3)	0.1679(7)	6.4(1)
C(10)	0.5714(6)	0.5793(3)	0.2456(7)	6.9(1)
C(11)	0.6502(5)	0.5148(3)	0.2853(6)	6.2(1)
C(12)	0.5646(6)	0.4437(3)	0.2430(7)	6.4(1)

The atoms are given in the form of the isotropic equivalent displacement parameters defined as:  $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ .

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